Waste Management 31 (2011) 705–713

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Exergy analysis of the Chartherm process for energy valorization and material recuperation of chromated copper arsenate (CCA) treated wood waste

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ARTICLE INFO

Article history:
Received 4 June 2010
Accepted 2 December 2010
Available online 30 December 2010

ABSTRACT

The Chartherm process (Thermya, Bordeaux, France) is a thermochemical conversion process to treat chromated copper arsenate (CCA) impregnated wood waste. The process aims at maximum energy valorization and material recuperation by combining the principles of low-temperature slow pyrolysis and distillation in a smart way. The main objective of the exergy analysis presented in this paper is to find the critical points in the Chartherm process where it is necessary to apply some measures in order to reduce exergy consumption and to make energy use more economic and efficient. It is found that the process efficiency can be increased with 2.3–4.2% by using the heat lost by the reactor, implementing a combined heat and power (CHP) system, or recuperating the waste heat from the exhaust gases to preheat the product gas. Furthermore, a comparison between the exergetic performances of a 'chartherisation' reactor and an idealized gasification reactor shows that both reactors destroy about the same amount of exergy (i.e. 3500 kW kg_{wood}^{-1}) during thermochemical conversion of CCA-treated wood. However, the Chartherm process possesses additional capabilities with respect to arsenic and tar treatment, as well as the extra benefit of recuperating materials.

1. Introduction

On a world-wide scale, the wood preservation industry treats approximately 30 million m^3 of wood each year. Two-thirds of this volume has been treated with chromated copper arsenate (CCA) (Humphrey, 2002). CCA has been used to preserve wood from insects, fungi and water damage for many years. Applications include telephone poles, railway sleepers, timber from landscape and cooling towers, wooden silos, hop-poles, cable drums and wooden play-ground equipment. CCA is still used today (however almost exclusively as oxides and for industrial applications), regardless of the growing disposal problem encountered in Europe, the United States and Japan (Helsen, 2009). The CCA-treated wood waste is classified as hazardous in the EU and consequently subject to stringent requirements. The quantities of discarded CCA-treated wood are expected to increase significantly in the future (Solo-Gabriele et al., 2003). In order to reduce this growing amount of wood waste, it is necessary to develop environmentally friendly recuperation and/or disposal techniques. Controlled landfilling is still the preferred disposal method for CCA-treated wood waste in the US. However, wood has a large calorific value hence its energetic content should be valorized prior to disposal. Helsen and Van den Bulck (2005) identified possible candidates for the thermochemical treatment of CCA wood. Pyrolysis (slow and flash), incineration, co-incineration and gasification were evaluated in their study with emphasis on environmental performance and the possibility for energy and/or material recuperation. In Europe, alternative technologies such as gasification (XYLOWATT, online) and slow pyrolysis are in a demonstration phase. Incineration plants with extensive gas cleaning are current practice.

The numerous studies and experiments that have been carried out on burning contaminated wood reflect three common points. The combustion of CCA-treated wood waste emits highly toxic smoke and fumes in the environment. The municipal waste incinerators, and most of the industrial waste incinerators, are not equipped to retain this type of toxic elements, especially at the concentrations involved. Mixing of the polluted wood with other waste streams causes the destabilization of the combustion conditions in the incinerators, resulting in the appearance of highly toxic and difficult to control chemical compounds.

It has been reported (Wilkins and Murray, 1980; Dobbs et al., 1978; Marutzky, 1990) that 8–95% of arsenic (As(III)) is volatilized upon burning of CCA-treated wood. Conventional (fast) pyrolysis processes operate at too high temperatures to prevent the release of gaseous arsenic to air. Moreover, part of the arsenic is concentrated in the liquid pyrolysis oil.

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doi:10.1016/j.wasman.2010.12.001

Nomenclature

daf	dry and ash free
b	specific exergy (kJ kg^{-1})
$\bar{b}$	specific molar exergy (kJ mol^{-1})
B	exergy (kJ)
h	specific enthalpy (kJ kg^{-1})
HHV	higher heating value (kJ kg^{-1})
LHV	lower heating value (kJ kg^{-1})
$\dot{m}$	mass flow (kg s^{-1})
MW_g	average molecular weight gas mixture (kg mol^{-1})
P	pressure(kPa)
$\dot{Q}$	heat flow (kW)
R	universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1})
s	specific entropy (kJ kg^{-1} K^{-1})
T	temperature (K)
y	molar fraction (–)
z	mass fraction (–)

Greek symbols

β	ratio of the chemical exergy to the lower heating value of the dry matter (–)
η_b	exergy efficiency (%)
μ	chemical potential (kJ mol^{-1})

Sub and superscripts

ch	chemical
CV	control volume
D	destroyed
e	outlet
g	gas
i	inlet
ph	physical
S	sulphur
0	(subscript) surroundings
0	(superscript) standard

On the other hand, low-temperature pyrolysis might offer a promising solution to the growing disposal problem. Since low temperatures and no oxidizing agents are used, metal release is significantly reduced in comparison to combustion. Moreover, it is possible to recover the metals from the solid pyrolysis residue (char). The Chartherm process has been identified as a candidate for the best available technology to treat CCA-impregnated wood waste (Helsen and Van den Bulck, 2005). This thermochemical conversion process combines the principles of low-temperature pyrolysis and distillation. It aims at a maximum recuperation of the metals, carbon and energy contained in the CCA-treated wood waste.

A simplified scheme of the Chartherm process is presented in Fig. 1. The complete process can be divided into three sections (Helsen, 2009): crushing, 'chartherisation' (thermochemical conversion) and separation (or refining). The process operates semi-continuously, at start-up the reaction column is filled with wood chips and during operation extraction of hot charcoal at the bottom occurs simultaneously with the supply of cold wood at the top of the reactor, ensuring continuous operation of the system. The crushed wood is heated by a flow of hot inert gases in counter flow regime, which means the wood is exposed to a temperature gradient when it moves downwards. The upward gas stream has an important function to fulfil, apart from supplying heat to the reactor. The gas flow takes the vapours, released during wood decomposition, from the hot zone (370–390 °C) at the bottom of the reactor to the cooler zone (60 °C) near the top. While moving upwards, the heavy organic compounds are condensed, followed by another cycle of heating, cracking, evaporation, etc. while moving downwards again. Conventional gasification and pyrolysis of wood produce a sticky tar fraction which can cause maintenance (and consequently performance) problems (e.g. fouling of heat exchanger). However, the temperature gradient in the 'chartherisation' reactor and the restriction of the hot zone to a thin region (i.e. typically around 5% of the reactor height) at the bottom of the reactor result in operating conditions characterized by near-zero tar and/or arsenic emissions.

While the wood is dried and decomposed, volatile combustible vapours are released and a coal-type residue (charcoal) that entraps the metals and minerals is produced. The volatile combustible gases, free of metals, leave at the top of the reactor where they are washed by a water scrubber (to capture pollutants if needed, e.g. in case of disturbances) and subsequently burned in a gas burner that supplies energy to the system. The charcoal product is cooled, compressed to powder and fed to the subsequent separation stage. In order to obtain a clean carbon product on the one hand, and a powder containing the metals, minerals and some carbon on the other hand, centrifugal separation is applied. More detailed information about the Chartherm process is published by Helsen (2009).

'Chartherisation' differs from conventional low-temperature pyrolysis since the pressure and temperature decrease stepwise with the height of the wood column, similar to a distillation column. The vapours that are released during wood decomposition flow upward where part of them condenses due to the cooling effect of the wood column. These condensed compounds are cracked when they arrive again in the hot zone at the bottom of the column. The wood column acts both as a condenser and a filter in this sequence of evaporation, cooling, condensation, heating and cracking. Additionally, it causes a pressure drop over the reactor. As a result, only a solid and a gaseous product are formed.

The purpose of this paper is to evaluate the Chartherm process by using exergy analysis. Exergy, first defined by Rant (1956), is a measure to define the quality of energy or better: *exergy is the portion of the total energy of a system that is available for conversion to useful work*. Exergy analysis is used to evaluate the efficiency of the energy-utilizing components of the process, and to detect quantitatively the causes of thermodynamic imperfection. Furthermore, measures that will improve the use of resources and the process efficiency are suggested.

2. Methodology

2.1. Exergy calculation

The quality of energy is measured by exergy. As energy is used in a process it loses quality, its exergy decreases. Exergy is defined as *the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interactions only with the above-mentioned components of nature* (Szargut et al., 1988). Energy is neither created nor destroyed during a process, it changes from one form to another (first law of thermodynamics). Exergy on the other hand, can be destroyed. This exergy destruction is due to process irreversibilities, characterized by an increase in entropy (second law of thermodynamics).

Exergy is definable and computable (in theory) for any substance or system, with respect to the environment in which the system is located (i.e. its surroundings). Five different types of exergy B [kJ] can be identified, namely potential, kinetic, physical, chemical and nuclear exergy (Ayres et al., 2006):

$$B = B_p + B_k + B_{ph} + B_{ch} + B_{nu} \quad (1)$$

Potential (B_p) and kinetic (B_k) exergy are equivalent to the corresponding energy terms, these two contributions can be disregarded for the exergy analysis of the Chartherm process. Nuclear exergy (B_{nu}) can also be disregarded. Physical exergy (B_{ph}) is the work obtainable by taking a substance through reversible physical processes from its initial state (temperature T, pressure P) to the state determined by the temperature T_0 and the pressure P_0 of the surroundings (Szargut et al., 1988). For the purpose of analyzing and optimizing (thermo)chemical processes on an industrial scale, chemical exergy (B_{ch}) plays a major role. Chemical exergy is the work that can be obtained by bringing a substance in a reversible way to the state of the reference substances in the reference environment at temperature T_0 and pressure P_0 (Szargut et al., 1988). It consists of two contributions (Rivero and Garfias, 2006): reactional exergy results from the chemical reactions necessary to produce species existing as stable components in the environment, from the initial composition of the substance; concentrational exergy results from the necessary processes to match the chemical concentration of the produced species to their chemical concentration in the environment.

The above-mentioned definitions illustrate the importance of defining an appropriate reference system when calculating both physical and chemical exergy. The reference system defines the state of mutual equilibrium between the system of interest and its surroundings. It includes parameters for the environment in which the system operates, in terms of temperature, pressure and chemical composition. In reality, however, the actual environment is not in equilibrium and therefore, a number of simplifying approximations need to be made.

In order to calculate physical exergy there are no difficulties associated with defining an appropriate reference level for temperature and pressure, these are set to ambient atmospheric temperature and pressure. In this work, these are taken as 25 °C and 1 atm, respectively.

For the calculation of chemical exergy, the choice of a reference system is not as straightforward. It requires detailed knowledge of the average chemical composition of the reaction products but also of the environmental sink with which the system interacts. In the present work, the methodology proposed by Szargut et al. (1988) is followed. For every chemical element, a reference species is defined. These reference species are the most abundant components of the natural surroundings and are assigned the lowest chemical exergy (e.g. the molecule CO_2 is chosen for the element C, H_2O for H and O_2 for O). Szargut's approach recognises that the three main environmental sinks (i.e. atmosphere, oceans and Earth's crust) are not in mutual equilibrium, but assumes the reaction products must go to one of these three sinks, depending on whether they are volatile (to air), soluble in water (to oceans) or neither (to crust). In order to simplify, Szargut suggests that the chemical exergy obtained in standard conditions, i.e. an ambient temperature of 25 °C and an atmospheric pressure of 1 atm, should be considered as a standard chemical exergy. Standard chemical exergies for chemical compounds and pure elements can be found in the literature (Szargut et al., 1988; Szargut, 2005; Bejan et al., 1996).

Exergy can be transferred by work, heat and matter. From the definition of exergy, mechanical work is identical to the physical work exergy. The exergy of heat (B_Q [kJ]), or the maximal possible conversion of heat to work, depends on the temperature at which heat is available (T_{source} [K]) and the temperature level at which the reject heat can be disposed (i.e. the temperature of the surroundings T_0 [K]):

$$B_Q = \left(1 - \frac{T_0}{T_{source}}\right) \cdot Q \quad (2)$$

The exergy B of a material flow with enthalpy H [kJ] and entropy S [kJ K^{-1}], crossing the boundaries of an open system, can be written as the sum of three terms (Ayres et al., 2006):

$$B = (H - H_0) - T_0(S - S_0) - \sum \mu_i (N_i - N_{i,0}) \quad (3)$$

with μ_i [kJ mol^{-1}] being the chemical potential of the ith component and N_i [mol] the number of moles of this component. The first and second term in Eq. (3) account for the transfer of physical exergy, the third term accounts for the chemical transformation of the system. If specific exergies (per unit mass flow) are used, the following expression is found:

$$b = b_{ph} + b^0_{ch} \quad (4)$$

with b_{ph} [kJ kg^{-1}] the specific physical exergy and b^0_{ch} [kJ kg^{-1}] the standard specific chemical exergy. As mentioned earlier, the standard specific chemical exergy of a material flow b^0_{ch} is determined by the standard chemical exergy of its constituents and by the concentration of the components in the mixed stream. If the mixture can be considered an ideal gas (valid for all gas streams in the Chartherm process), its standard chemical exergy is given by:

$$b^0_{ch,g} = \frac{\bar{b}^0_{ch,g}}{MW_g} \quad (5)$$

with MW_g [kg mol^{-1}] the average molecular weight of a gas mixture and $\bar{b}^0_{ch,g}$ [kJ mol^{-1}] its standard specific chemical exergy on a molar basis:

$$\bar{b}^0_{ch,g} = \sum_i y_i \bar{b}^0_{ch,i} + RT_0 \sum_i y_i \ln y_i \quad (6)$$

with y_i the molar concentration of component i, $\bar{b}^0_{ch,i}$ the standard chemical exergy of component i (available in the literature, e.g. Rivero and Garfias (2006)) and R the ideal gas constant [8.314×10^{-3} kJ mol^{-1} K^{-1}].

It is important to bring the gas in physical equilibrium with the surroundings before applying Eq. (6) since this may affect the physical state of water (liquid or vapour) in the mixture and hence influence its chemical exergy.

The chemical exergy of a mixture is always lower than the sum of the exergy values of its individual components, which is explained by the negative value of the mixing exergy (second term on the right hand side of Eq. (6)).

The molecular composition of liquid and solid organic wastes is often not known, which makes it impossible to determine the exact chemical exergy of the waste input stream. Therefore, the statistical correlation of Szargut and Styrylska (1964) is used to approximate the standard chemical exergy of solid biomass fuel (e.g. wood chips). The chemical exergy of solid fuels is not only determined by the lower heating value LHV (i.e. net enthalpy of combustion), but also by the water, sulphur and ash content of the fuel:

$$b^0_{ch,wood} = z_{org} \cdot \beta \cdot LHV_{org} + z_S \cdot (b^0_{ch,S} - LHV_s) + z_{H_2O} \cdot b^0_{ch,H_2O} + z_{ash} \cdot b^0_{ch,ash} \quad (7)$$

with $b^0_{ch,wood}$, $b^0_{ch,s}$, b^0_{ch,H_2O}, and $b^0_{ch,ash}$ the standard (specific) chemical exergy [kJ kg^{-1}] of wood, sulphur, water and ash, respectively. z_{org} z_S z_{H_2O} and z_{ash} are the weight fractions of organic components, sulphur, water and ash, respectively in the wood. LHV_{org} is the lower heating value of the organic fraction contained in the wood

[18,807 kJ kg^{-1}], LHV_S is the lower heating value of sulphur [9163 kJ kg^{-1}].

The factor β [−] expresses the ratio of the chemical exergy to the lower heating value of dry organic substances, as a function of the elemental contents. It is given by the following formula:

$$\beta = \frac{1.0412 + 0.216\frac{z_{H_2}}{z_C} - 0.2499\frac{z_{O_2}}{z_C}\left[1 + 0.7884\frac{z_{H_2}}{z_C}\right] + 0.045\frac{z_{N_2}}{z_C}}{1 - 0.3035\frac{z_{O_2}}{z_C}},$$

$$\text{for } 0.667 \leqslant \frac{z_{O_2}}{z_C} \leqslant 2.67 \tag{8}$$

2.2. System approach

The application of exergy analysis to a system is based on the block method (Rivero and Anaya, 1997). The system is assumed to consist of a combination of black boxes that can interact with the surroundings in three ways only: by mass transfer, heat transfer and work transfer. Mass transfer includes the input of raw materials and utilities, and the output of products and waste. Work and heat transfer are represented by the energy needs (e.g. electricity, mechanical work), and by the energy outputs and waste heat streams.

The first step in the application of an exergy analysis consists of representing the system by a series of interconnected blocks. Inputs and outputs of each block represent the main process parameters, among them the exergy value of each stream connected to the block. A simplified block diagram for the Chartherm process is presented in Fig. 1, with the legend given in Table 1.

Once the block diagram has been constructed, and the system boundaries are clearly defined, it is possible to set up mass, energy and entropy balances. This is done separately for each block, and globally for the entire system. Therefrom, exergy balances and exergy performance parameters can be obtained.

It was mentioned earlier that exergy, like energy, can be transferred by work, heat and matter. Unlike energy however, exergy can also be destroyed. Exergy destruction ($\dot{B}_D$ [kW]) is the result of the irreversibility of the processes taking place in the system. It is calculated as the difference between the total exergy input $\dot{B}_{in}$ and the total exergy output $\dot{B}_{out}$, or by using the Gouy-Stodola theorem (Bejan, 1995):

$$\dot{B}_D = \dot{B}_{in} - \dot{B}_{out} = T_0 \Delta \dot{S} \tag{9}$$

The total exergy output is the sum of the useful exergy and the exergy that is lost to the surroundings through heat transfer. Fig. 2 gives a schematic representation of Eq. (9) which states that the rate at which exergy is transferred into the control volume must exceed the rate at which exergy is transferred out. The difference is the rate at which exergy is destroyed within the control volume due to irreversibilities and the rate at which exergy is lost due to heat loss to the environment. At steady state, the exergy rate balance for an open system takes the form:

$$0 = \sum_j \dot{B}_{Q,j} - \dot{W}_{CV} + \sum_i \dot{B}_i - \sum_e \dot{B}_e - \dot{B}_D \tag{10}$$

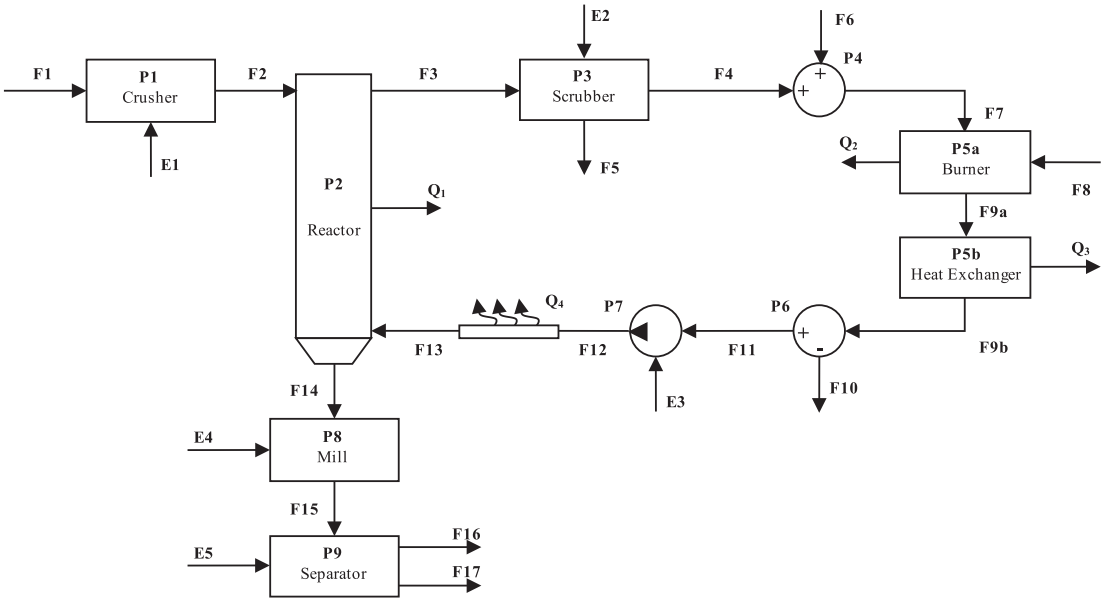

Fig. 1. Simplified scheme of the Chartherm process (F: mass flow, Q: heat flux, E: electric power).

Table 1
Legend to Fig. 1 (F: mass flow, Q: heat flux, E: electric power).

Symbol	Description	Symbol	Description	Symbol	Description
F1	Wood poles	F7	Mixed product gas	F12	Compressed combustion gas
F2	Wood chips	F8	Propane–air mixture	F13	F12, including pipe heat losses
F3	Product gas	F9a	Combustion gas	F14	Synchar
F4	Dried product gas	F9b	Cooled combustion gas	F15	Crushed synchar
F5	Water	F10	Exhaust gas	F16	Carbon™ (carbon product)
F6	Air	F11	F9b	F17	Agglomerates (metals and minerals)
E1	Wood crusher	E5	Separator	Q1	Reactor heat loss
E2	Scrubber	E6	Peripheral electrical instrument	Q2	Burner heat loss
E3	Compressor			Q3	Heat exchanger heat load
E4	Mill			Q4	Pipe heat losses

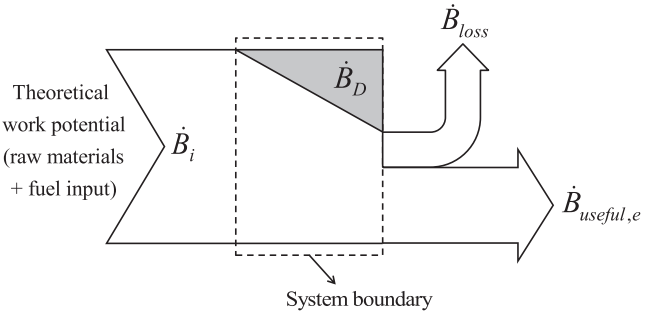

Fig. 2. Schematic diagram of the exergy balance for an open system.

Table 2
Process conditions used in the exergy analysis of the Chartherm process (pressures are gage pressures).

Property	Value	Property	Value
T_{F13} (°C)	370	$\dot{m}_{F1}$ (kg h^{-1})	1500
T_{F3} (°C)	60	$\dot{m}_{propane}$ (kg h^{-1})	87
P_{F13} (Pa)	4903	$\dot{V}_{F12}$ (Nm^3 h^{-1})	2940
P_{F3} (Pa)	98	ΔT_{pipe} (°C)	30

Table 3
Wood properties taken from the Phyllis database (ECN, online).

Property	Value	Property	Value
z_{org} (wt.%)	80.7	C (wt.% daf)	51.6
z_{ash} (wt.%)	4.8	H (wt.% daf)	6.05
z_{H_2O} (wt.%)	14.5	O (wt.% daf)	41.2
LHV_{org} (kJ kg^{-1}org)	18,807	N (wt.% daf)	1.18
HHV_{org} (kJ kg^{-1}org)	20,170	S (wt.% daf)	0.12

where $\dot{B}_i$ and $\dot{B}_e$ are exergy transfer rates [kW] at inlets and outlets, respectively. $\dot{B}_{Q,i}$ represents the exergy transfer by heat between the control volume and its surroundings, $\dot{W}_{CV}$ represents the exergy transfer by work between the control volume and its surroundings, this term is equal to zero for the Chartherm process.

Exergy efficiency η_b, also known as second-law efficiency, computes the efficiency of a process taking the second law of thermodynamics into account. It is calculated as the ratio of the useful exergy output to the net supplied exergy:

$$\eta_b = \frac{\sum B_{e,useful}}{\sum B_i} \quad (11)$$

The destruction of exergy is closely related to the creation of entropy. Hence, any system containing highly irreversible processes will have a low exergy efficiency.

It is not always trivial to determine the useful exergy output of (sub)processes. If, for example, the waste heat of a component is utilized elsewhere in the global process, its exergy is called useful. If, in contrast, the waste stream would be rejected to the surroundings, its exergy would be lost, and is thus not useful. From a global system perspective, individual component heat losses are thus not necessarily exergy losses. Irreversibilities, on the other hand, contribute to exergy destruction and hence always have a negative impact on the global process exergy efficiency.

In order to analyze the Chartherm process thermodynamically, the following assumptions have been made:

1. Steady state and continuous operation for all units.
2. Kinetic and potential energy changes of mass flows are neglected.
3. Environmental conditions are set to 25 °C and 1 atm.
4. All gases are considered ideal.

Table 4
Molar composition (mol%) of gas streams in the Chartherm process (nomenclature as in Fig. 1).

	Formed in reactor	F3	F4	F7	F9a	F9b	F13
$H_2O_{(g)}$	22.1	19.7	19.7	18.2	18.8	18.8	18.8
$H_2O_{(l)}$	45.3	11.7	0.0	0.0	0.0	0.0	0.0
N_2	7.9	50.1	58.6	60.3	64.7	64.7	64.7
O_2	5.3	1.5	1.7	3.0	0.1	0.1	0.1
H_2	1.1	0.3	0.3	0.3	0.0	0.0	0.0
CO	6.6	1.7	2.0	1.9	0.0	0.0	0.0
CO_2	8.5	14.3	16.8	15.5	16.4	16.4	16.4
CH_4	3.2	0.8	1.0	0.9	0.0	0.0	0.0

5. No pressure drop over heat exchangers.
6. The heat loss through pipes is represented by a temperature decrease of 30 °C for the gas stream.

A summary of the process conditions as used in the exergy analysis is given in Table 2. The properties of wood are taken from the Phyllis database (ECN, online), and repeated here as Table 3. Detailed calculations can be found in Vanden Auweele (2009).

3. Results

3.1. Identification of gas flows

The first part of the analysis consists of identifying the gas flows for all units (shown in Fig. 1) that make up the Chartherm process. It is assumed that during 'chartherisation', the wood chips are completely converted into combustible gases (67 wt.%) and charcoal (33 wt.%) (Helsen, 2000). The composition of the gases exiting the reactor, and that of the gases entering the reactor are based on measurements performed by Thermya (Bordeaux, France). Using these experimental data, the composition of the gas flows entering and exiting the other units is determined. Table 4 displays the results and shows that a significant amount of liquid water is generated in the reactor. As a consequence, the gas stream exiting the reactor contains water droplets. It is assumed that the scrubber coupled to the reactor outlet removes all liquid water from the product gas, and hence delivers a saturated gas stream.

The oxygen supply to the reactor is limited in order to maintain a reducing environment inside the 'chartherisation' reactor. Therefore, the oxygen level of the gas stream entering the reactor (F13) is kept below 0.1 mol% by adjusting the amount of air (F6) that is mixed with the product gas (F4) before entering the gas burner.

3.2. Energy balance

Fig. 3 provides a schematic view of the global Chartherm process, indicating input and (useful) output streams. The input

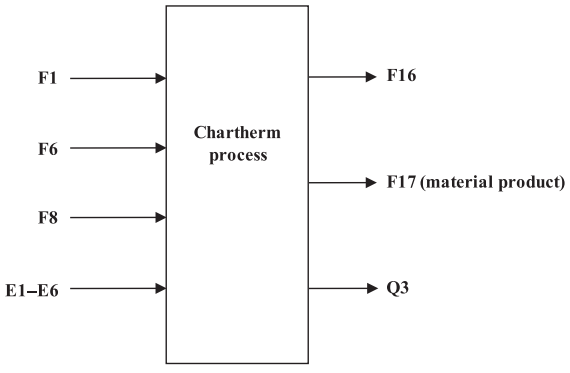

Fig. 3. Global Chartherm process with input and (useful) output streams.

streams to the global Chartherm process consists of the wood feed (F1), the sum of the electrical inputs (E1 + . . . + E6), the propane–air mixture supplied to the burner (F8) and the amount of air (F6) mixed into the product gas in the burner mixing chamber. The energy content of this last stream (F6) equals zero since the supplied air is assumed to consist of 79% nitrogen and 21% oxygen, these two components have a standard enthalpy of formation of zero. Useful output streams consist of the carbon product (F16), agglomerates (F17) and the heat exchanger heat load ($\dot{Q}_3$, used for steam production). The powder (F17), which is recovered from the charcoal product, contains valuable metals and minerals, besides a small amount of carbon since the separation technique cannot reach 100% efficiency and the priority is to obtain a pure carbon product (Corban™, F16). Output stream F17 could be valorized energetically, but since the metals and minerals posses a high material recycling value it is considered to be a useful *material* output instead of an *energy* output. The carbon product (F16) on the other hand, is assumed to serve as a fuel (i.e. energy valorization). Alternatively, Corban™ could be used for active carbon production (i.e. material valorization).

The Sankey diagram shown in Fig. 4 graphically represents the global energy balance for the steady-state Chartherm process. The total energetic power input is nearly 8000 kW and the useful output is approximately 4900 kW, resulting in an energy efficiency of 61.2%. In order to determine the energy input of wood (F1), the higher heating value is used since the product gas leaves the reactor at approx. 60 °C thus the latent heat of condensation needs to be included. Heat losses to the surroundings caused by temperature differences are determined for the reactor ($\dot{Q}_1$=1067 kW), the burner ($\dot{Q}_2$=118 kW) and the piping system ($\dot{Q}_4$=38 kW). Additionally, sending the exhaust gases (F10) to a stack results in an energy loss to the surroundings of 468 kW. The energy recovered from the heat exchanger after the burner ($\dot{Q}_3$ = 884 kW) can be used for various applications. Here, the production of steam (800 kg h^{-1}) at 790 °C (20 bar) is considered. The pumping power required to bring the water from atmospheric pressure to 20 bar is small (0.4 kW) and hence neglected in the global process energy and exergy efficiency calculations. The energy flow *Other losses* accounts for the possible underestimation of certain energy losses due to a lack of experimental data and closes the energy balance.

Detailed calculations can be found in Vanden Auweele (2009).

3.3. Exergy analysis

The equations from Sections 2.1 and 2.2, and the results from the identification of gas flows are used to determine the exergy of the flows considered in the Chartherm process. The exergy content of the air flow (F6) equals zero since the supplied air is at reference conditions. Table 5 summarizes the results.

Fig. 5 shows the global exergy balance for the Chartherm process, presented as a Sankey diagram. The total exergy input to the Chartherm process is nearly 8400 kW and the useful output is approx. 4500 kW, resulting in an exergy efficiency of 54.1%. The heat losses are less important in the exergy balance than in the energy balance (sum of 520 kW versus 1220 kW, resp.). This illustrates how the energy quality of heat is related to the temperature at which it is available; the maximum possible conversion of heat to work decreases with a decreasing heat source temperature.

The exergy destructions in the different units stem from one or more of three principal irreversibilities associated with chemical reaction, heat transfer and friction (Bejan et al., 1996). The exergy destruction data are summarized in Table 6. The 'chartherisation' reactor appears to be the most important source of irreversibility,

Table 5
Specific physical and chemical exergy of the material flows in the Chartherm process.

	$\dot{m}$ (kg h^{-1})	T (K)	P (MPa)	b_{ph} (kJ kg^{-1})	b^0_{ch} (kJ kg^{-1})	$\dot{B}$ (kW)
F1	1500	298	0.101	0	17,038	7099
F2	1500	298	0.101	0	17,038	7099
F3	4750	333	0.101	205	528	966
F4	4290	333	0.101	21	579	714
F5	460	333	0.101	8	6	2
F6	351	333	0.101	2	4	1
F7	4641	330	0.101	18	532	709
F8	1590	298	0.101	0	2663	1176
F9a	6231	1073	0.101	504	97	1040
F9b	6231	673	0.101	171	97	462
F10	2486	673	0.101	171	97	184
F11	3745	673	0.101	171	92	274
F12	3745	673	0.106	175	92	278
F13	3745	643	0.106	155	97	262
F14	495	298	0.101	0	32,870	4520
F15	495	298	0.101	0	32,870	4520
F16	438	298	0.101	0	34,125	4152
F17	57	298	0.101	0	27,049	428

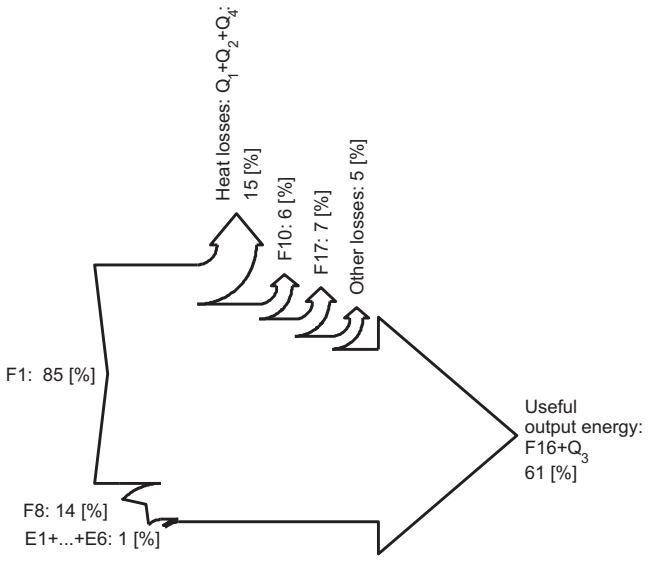

Fig. 4. Sankey diagram – Energy balance for the Chartherm process (100% = 8000 kW).

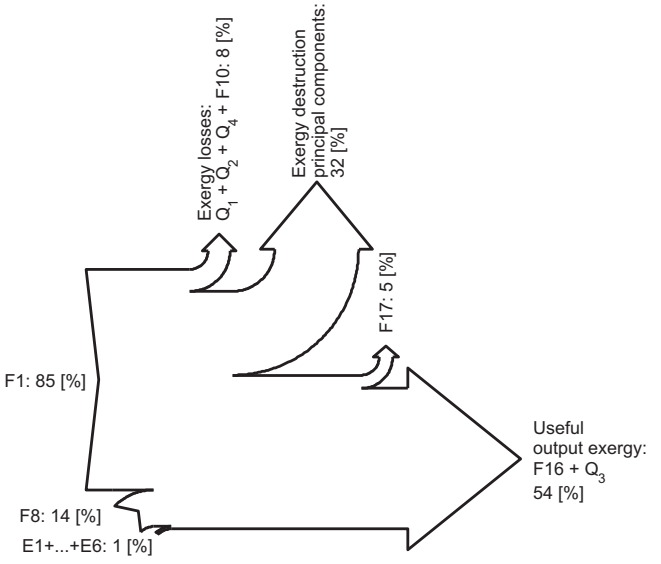

Fig. 5. Sankey diagram – exergy balance for the Chartherm process (100% = 8400 kW).

with the most significant irreversibility related to the chemical reactions intrinsic to the Chartherm process. It should be noted that prior to changing process conditions to decrease exergy consumption during 'chartherisation', all chemical, thermodynamic and transport processes (including their dependency on process parameters) need to be fully understood. Despite the irreversibilities occurring in the 'chartherisation' reactor, it is characterized by a relatively high exergy efficiency, i.e. 75%, and thus a low exergy loss.

The gas burner has a lower exergy efficiency and destroys a considerable amount of exergy, which is inherent to burners (Taniguchi et al., 2005). In Section 3.5, several ways to increase the global process exergy efficiency based on burner and/or reactor improvements are discussed.

The exergy efficiency of the heat exchanger depends on the way the energy (in the form of heat) is further exploited. If the energy is utilized to generate steam at 790 °C and 20 bar, the exergy efficiency of the heat exchanger equals 65%. If, in contrast, the energy is used to heat feed water (e.g. from 25 to 80 °C), the exergy efficiency drops below 15%.

Detailed calculations can be found in Vanden Auweele (2009), the key results are summarized in Tables 6–10.

Table 6
Results of the exergy analysis for the most important units in the Chartherm process.

	$\dot{B}_i$ (kW)	$\dot{B}_{useful,e}$ (kW)	$\dot{B}_{loss}$ (kW)	$\dot{B}_D$ (kW)	η_b (%)
Reactor	7361	5486	415	1827	74.5
Burner	1898	1040	85	772	54.8
Heat exchanger	578	374	0	204	64.7
Global process[a]	8363	4525	706	3131	54.1

[a] Global process exergy loss and destruction includes exhaust to stack and pipe heat losses.

Table 7
Results of the exergy analysis with process improvements: recovery of reactor heat loss $\dot{Q}_l$ by steam production.

	$\dot{B}_i$ (kW)	$\dot{B}_{useful,e}$	$\dot{B}_{loss}$	$\dot{B}_D$	η_b
Reactor	7361	5486	125	1750	74.5
Burner	1898	1040	85	772	54.8
Heat exchanger (after burner)	578	374	0	204	64.7
Global process	8363	4801	415	3146	57.4

Table 8
Results of the exergy analysis with process improvements: recovery of heat from the flue gases by means of a waste heat recovery system (WHRS).

	$\dot{B}_i$ (kW)	$\dot{B}_{useful,e}$ (kW)	$\dot{B}_{loss}$ (kW)	$\dot{B}_D$ (kW)	η_b (%)
Reactor	7373	5504	417	1452	74.6
Burner	1515	972	40	503	64.2
Heat exchanger (after burner)	532	344	0	188	64.7
Heat exchanger (WHRS)	76	40	0	35	53.3
Global process	7970	4496	552	2922	56.4

Table 9
Results of the exergy analysis with process improvements: combined heat and power (CHP) system for electricity and heat generation.

	$\dot{B}_i$ (kW)	$\dot{B}_{useful,e}$ (kW)	$\dot{B}_{loss}$ (kW)	$\dot{B}_D$ (kW)	η_b (%)
Reactor	7378	5509	417	1451	74.7
CHP gas engine	1439	753	175	510	52.3
Heat exchanger (after burner)	*No longer required*				
Global process	7889	4467	756	2666	56.6

Table 10
Results of the exergy analysis with process improvements: combination of CHP and WHRS.

	$\dot{B}_i$ (kW)	$\dot{B}_{useful,e}$ (kW)	$\dot{B}_{loss}$ (kW)	$\dot{B}_D$ (kW)	η_b (%)
Reactor	7404	5541	420	1443	74.8
CHP gas engine	1087	657	124	306	60.5
Heat exchanger (WHRS)	51	22	0	29	43.3
Heat exchanger (after burner)	*No longer required*				
Global process	7515	4379	623	2513	58.3

3.4. Benchmarking against gasification

The 'chartherisation' reactor is compared thermodynamically with a gasification reactor, since both can be used for thermochemical conversion of wood. The exergy efficiency of the gasification reactor is taken from a study (Ptansinski et al., 2007) that evaluates an idealized gasifier (i.e. chemical equilibrium is reached, ashes are not considered and heat losses are neglected). For this reason, the comparison that is made here focuses solely on exergy destruction in the reactor, without taking into account exergy losses and other units within the global system. The wood input to the gasification reactor is almost identical to the wood input used for the analysis of the Chartherm process. Both reactors are fed with treated wood, the wood properties are taken from the Phyllis database. Slight variations are due to database updates (2007 versus 2010).

The 'chartherisation' reactor is found to be exergetically equally efficient as the gasification reactor, the destroyed exergy equals 3500 kW kg_{wood}^{-1} and 3370 kW kg_{wood}^{-1}, respectively. Some remarks have to be made about this result:

- Gasification calculations were performed for the carbon point, which is at 650 °C. This temperature is low for practical gasification. It should be kept in mind that the higher the reactor temperature is, the higher the heat losses are. However, Ptansinski et al. (2007) did not consider heat losses.
- Gasification offers no solution for the arsenic problem, nor for the tar problem. Moreover, there is no opportunity for material recuperation.

A global system comparison is required in order to provide conclusive results, but based on in-depth process knowledge 'chartherisation' appears to be more efficient than gasification for the thermochemical conversion of CCA-treated wood waste, with respect to both maximal energy valorization and material recuperation.

3.5. Suggestions for improvement

The exergy destruction in the Chartherm reactor is the most important source of exergy consumption. Exergy optimization of chemical reactions has previously been studied by Leites et al. (2003). In order to increase the exergy efficiency, one has to use methods which counteract the improvement of the products yield by decreasing the driving force (i.e. change in Gibbs free energy) of the (mostly) endothermic chemical reactions taking place in the 'chartherisation' reactor. However, applying the suggested measures (i.e. increasing the reactor pressure, decreasing the reactor temperature or increasing the reactor residence time) to the Chartherm process will influence all processes taking place, including the arsenic dynamic behaviour. Hence, full knowledge of all mechanisms influencing the arsenic behaviour is needed. Changing the reaction conditions could influence the type of chemical reactions occurring in the reactor, the rate at which they take place, or their thermodynamic equilibrium. It requires further research to suggest

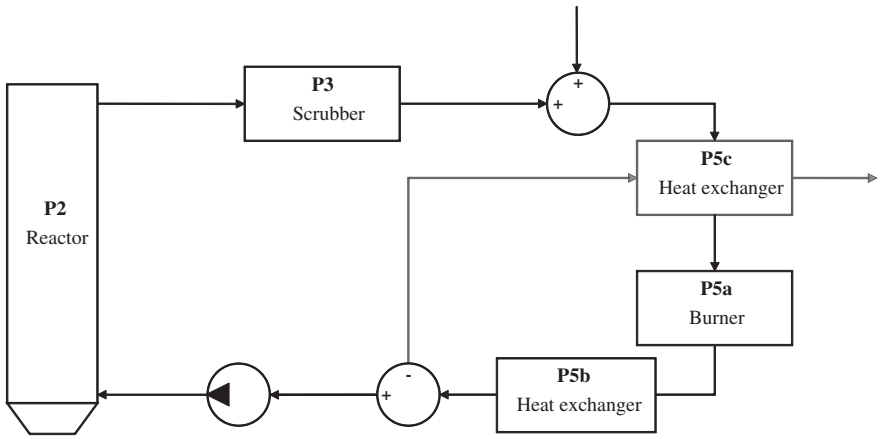

Fig. 6. Modified scheme for the Chartherm process: incorporation of a waste heat gas recovery system.

process improvements that will reduce the exergy destruction caused by irreversible chemical reactions occurring in the 'chartherisation' reactor. At present, the influence of elevated reactor pressure is being studied (Cuypers et al., 2009).

The reactor constitutes the most important heat loss in the global system. Reducing or recuperating this heat loss will improve the process efficiency and will consequently reduce burner propane requirements. The reactor heat loss could be reduced by insulation but this would influence operating conditions, i.e. the temperature gradient in the 'chartherisation' reactor and the restriction of the hot zone to a thin region at the bottom of the reactor. As mentioned in the introduction, these process characteristics are crucial to ensure near-zero tar and/or arsenic emissions, and should thus be maintained in order to ensure environmentally friendly operation.

Alternatively, the reactor heat loss could be recuperated by producing steam. This can be achieved by supplying the reactor heat loss $\dot{Q}_1$ to the heat exchanger that is located after the burner. In that case, 900 kg h^{-1} steam at 20 bar and 790 °C can be produced, which increases the global process exergy efficiency from 54.1% to 57.4%.

Inside the burner, air and fuel (propane) are mixed and burned to generate heat, some (F11) of which is transferred to the reactor. A large amount of the heat (F10) generated is wasted as exhaust or flue gases, which are removed via a stack. At this point, these gases still contain a considerable amount of thermal energy. The energy and exergy efficiency can be increased by using a waste heat gas recovery system to capture and use some of the energy contained in the flue gas. Among the different applications that use the heat contained in waste gases, load preheating has the highest potential efficiency (EERE, online). When the exhaust gases leaving the burner are brought into contact with a relatively cool load (F7, mixed product gas), energy will be transferred to this load, preheating it and reducing the fuel consumption in the burner. This is presented schematically in Fig. 6. If the exhaust gases are allowed to cool down to 120 °C during heat recovery (hence avoiding condensation), 30 kg h^{-1} propane can be saved. Hereby, the global process exergy efficiency increases from 54.1% to 56.4%.

Instead of feeding the Chartherm product gas (F4) to a burner, the energy contained in this stream could be used to generate electricity in combination with heat. The resulting combined heat and power system (CHP) would have a relatively low electric power output (<1 MWe) which is why a gas engine is chosen instead of a gas turbine (mostly used in the range of 1–100 MWe). The gas engine replacing the burner, is characterized by an electric efficiency of 25% and a thermal efficiency of 50%. Under the assumption that the compression cycle of the engine causes a sufficiently high temperature increase of the Chartherm product gas to allow for total combustion, propane consumption is decreased by 35 kg h^{-1}. Calculations show that the gas engine produces 315 kWe; this electric power can be sold to the grid or it can be used to provide the Chartherm process with the necessary electric energy. Furthermore, the extra heat exchanger is no longer required and the exergy efficiency of the process increases from 54.1% to 56.6%.

A combination of these two improvements, i.e. gas engine and waste heat gas recovery system, results in a global process exergy efficiency of 58.3%.

4. Conclusions

In the present study, the Chartherm process used for the energy valorization and material recuperation of CCA wood waste has been analyzed energetically and exergetically. The overall exergy system efficiency is calculated to be 54.1% with an exergy input of 8400 kW. The reactor consumes the largest amount of exergy. However, thermochemical reactions are inherent to the process and therefore, improving the exergy efficiency of the 'chartherisation' reactor is not straightforward. Several possible system improvements have been discussed:

- Steam generation by supplying the reactor heat loss to the heat exchanger located after the burner. Hereby, the process exergy efficiency increases to 57.4%.
- Recuperating the heat of the exhaust gases by using a waste heat recovery system lowers propane requirements by 30 kg h^{-1} and increases the global process exergy efficiency to 56.4%.
- Using a gas engine to generate heat and power will increase the exergy efficiency to 56.6%, meanwhile producing about 315 kW electric power.
- Combining a waste heat recovery system with combined heat and power generation increases the process exergy efficiency to 58.3%.

It is interesting to note that the difference in exergy destruction between 'chartherisation' and idealized gasification (at the carbon point) of CCA-treated wood is nearly the same. However, caution is required when comparing the global system. The Chartherm process offers a solution for the arsenic and tar problem (by the distillation process), as opposed to the gasification system where additional cleaning units must be introduced to deal with these problems. Moreover, gasification of wood waste results in energy recovery only; the Chartherm process offers the possibility to

recover both energy and valuable materials (heavy metals and carbon).

Acknowledgments

The authors would like to acknowledge the funding of the Ph.D study by the Research Fund K.U. Leuven. The authors are also grateful to Mr. D. Mateos from Thermya for providing the necessary data needed to carry out an exergy analysis of the Chartherm process.

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